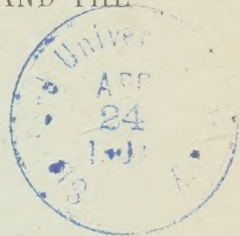


AN INVESTIGATION OF THE BORIDES AND THE
SILICIDES



BY

OLIVER PATTERSON WATTS

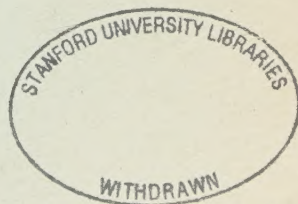
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A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
UNIVERSITY OF WISCONSIN
1905

(REPRINTED FROM THE BULLETIN OF THE UNIVERSITY OF WISCONSIN
ENGINEERING SERIES, VOL. 3, PP. 251-318)

MADISON, WISCONSIN

1906



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BY

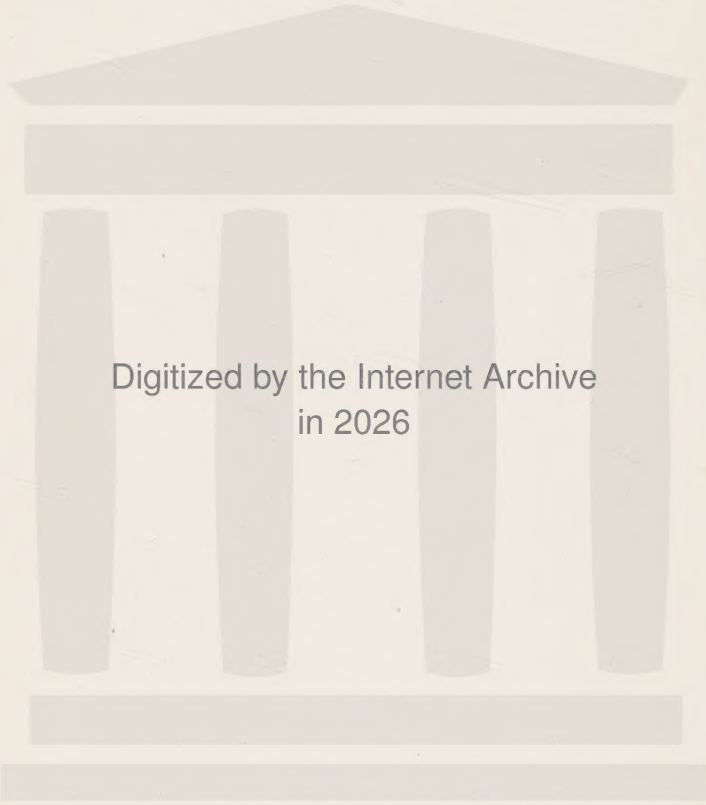
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PREFACE.

During the last two decades, notable contributions have been made to the field of chemistry through the use of the electric furnace. The high temperatures, made available by the conversion of electrical into thermal energy, have resulted in the discovery of a host of new compounds, and the duplication by art of various of nature's processes.

Among the compounds which play a prominent part in this "new chemistry of high temperatures," are the borides and the silicides; and it is the purpose of this paper to present the results of an experimental investigation of some of these compounds, together with a brief, yet comprehensive, account of these two series of chemical compounds, which have become of scientific and commercial importance through the advent of the electric furnace.

The methods most generally used heretofore for the preparation of the borides and the silicides have been synthesis from the elements, and reduction of a metallic oxide by excess of boron or silicon. Either of these methods requires as a preliminary the preparation of the non-metal, a long and difficult task, particularly in the case of boron, the purification of which by the method of Moissan¹ took from ten to fifteen days at a minimum. It therefore seemed to the writer that an experimental investigation of the possibility of the preparation of the borides and the silicides from their commercially available oxygen compounds by a single reaction in the electric furnace would be of value. This is one of the problems of this

¹ C. R., 114: 392-7 (1892). Ann. de Chim., 6: 296-320 (1895).

investigation. A second problem was the production by means of the electric furnace of a new series of definite chemical compounds, the silico-borides.

For this investigation all the resources of the electrochemical department of the University of Wisconsin were put at the writer's disposal by Professor C. F. Burgess, who by this, and by his personal interest and encouragement, has placed the writer under lasting obligations, which are here gratefully acknowledged.

O. P. W.

Laboratory of Applied Electrochemistry,
University of Wisconsin,
May, 1905.

AN INVESTIGATION OF THE BORIDES AND THE SILICIDES.

I.

HISTORICAL OUTLINE.

The history of the borides may be said to begin with the discovery by Descostils in 1808² that platinum could be fused by heating it with borax and lamp-black. This gave a product that was hard, brittle, and crystalline, which, dissolved in acids, left a residue of boric acid. It was a full half century from this first recorded instance of the combining of platinum and boron, before a boride of platinum of definite composition was isolated.

Similarly in regard to the silicides, the first discovery was the mere fact of the combination of silicon with the metals, followed after many years by the isolation of definite chemical compounds. In 1810, Davy³ discovered that the earths, silica, alumina, and glucina, when heated with iron and potassium, yielded a brittle ingot of a crystalline texture, harder and whiter than iron. In 1812, Berzelius⁴ announced that a mixture of silica and carbon, heated in the presence of iron filings, gave a white metal which, attacked by acids, yielded silica. Boussingault⁵ found that steel could be made with silicon in

² Ann. de Chim., 67 : 68 (1808).

³ Ann. de Chim., I, 75 : 152.

⁴ Ann. de Chim., I, 81. 178.

⁵ Ann. de Chim., II, 16 : 10-16.

place of carbon; and that platinum, heated with carbon, took up silicon from the crucible, becoming brittle, harder, and less dense. The number of such alloys with boron and silicon increased, and finally crystalline compounds of definite composition were separated from them.

With the use of the electric furnace for scientific research, the isolation of new borides and silicides received a tremendous impetus. It was not the promise of great commercial value which caused this sudden and remarkable extension of these series, nor the fact that new borides and silicides were likely to have strange and marvellous properties; quite the contrary, —their family resemblance is so strong that nothing short of a chemical analysis serves to distinguish between certain members of both series. It was the fascination of exploring this new realm of high temperature chemistry that led to experimentation, and since, in addition to carbon, boron and silicon are the chief elements whose compounds with the metals are stable at electric furnace temperatures, the inevitable result was a great increase in the list of borides and silicides. The phosphides, arsenides, and sulphides are other series of compounds stable at electric furnace temperature, which are as yet only incompletely investigated.

The bulk of the original literature concerning the borides and silicides is contained in the German and French chemical periodicals, and is available in English only through brief abstracts scattered in various chemical journals, and in the two English translations of Moissan's "Le Four Electrique."

It has been the purpose of the writer to collect from the original sources and to set forth in the appended tables the most important physical and chemical properties of the borides and silicides in such form that the data may be useful to all experimenters in this field.

TABLE I.—*Action of the metals upon silicon.*⁶

Metals which do not form silicides.	Metals in which silicon dissolves at high temperatures, but separates again as crystals on cooling.
Aluminum. Antimony. Bismuth. Cadmium. Gold. Lead. Potassium. Silver. Sodium. Tin. Zinc.	Aluminum. ⁷ Silver. Antimony. Bismuth. Tin. ⁸ Zinc. ⁸ Lead. Gold. ⁹

⁶ Vigouroux, *Ann. de Chim.*, 12:5 (1897).⁷ Announced by Deville and Wöhler, *Ann. de Chim.*, III, 49:73 (1857).⁸ Announced by Deville and Caron, *Ann. de Chim.*, III, 67:435 (1863).⁹ Metals in second column, with the exception of gold, are arranged in order of their solvent power for silicon. Moissan and F. Siemens, *C. R.*, 138:1299 (1904). *Bull. Soc. Chim.*, 31-32:1015 (1904).

TABLE II.—*Physical Properties of the Borides and Silicides.*

	Literature and Discovery.	How Made.	Description.	Hard- ness.	Specific Gravity.
Al_2B_4	Wöhler & Deville, Ann. de Chim. 52:63-91 (1858).	$\text{K}_2\text{BF}_6 + \text{KCl} + \text{Al}$	thin coppery, hexagonal crystals.		
Al_2B_{24}	Wöhler & Deville, " " " " (Supposed to be Boron.)	$\text{K}_2\text{BF}_6 + \text{KCl} + \text{Al}$	black, thin leaves.	9+	2.53 at 17°
$\text{Al}_3\text{B}_{48}\text{C}_2$	Wöhler & Deville, " " " " (Supposed to be Boron.) Composition and formulae of last two due to Hampe, Ann., 183:90 (1876).	$\text{B}_2\text{O}_3 + \text{Al}$	yellow crystals.	9+	2.61
BaB_6	Moissan & P. Williams, C. R., 125:629-34 (1897); Bull. Soc. Chim., 17:1015-20 (1897).	$\text{B}_2\text{O}_3 + \text{BaO} + \text{Al} + \text{C}$	small regular cryst.	9+	4.26 at 15°
$\text{Be}_6\text{B}_6\text{C}_4$	Lebeau, C. R., 126:1347-9 (1898)	$\text{BeO} + \text{B}$ in carbon crucible.	brilliant metallic cryst.		2.4
CaB_6	Moissan & Williams, C. R., 125:629-34 (1897); Bull. Soc. Chim., 17:1015-20 (1897).	$\text{B}_2\text{O}_3 + \text{CaO} + \text{Al} + \text{C}$	transparent cubic or rectangular cryst.	9+	2.33 at 15°
CB	O. Mulhauser, Z. anorg. Chem., 5:92 (1894).	$\text{B}_2\text{O}_3 + \text{C}$	bluish black, greasy feeling, malleable.		
CB_6	Moissan C. R., 118:556 (1894); Ann. de Chim., 9:280-6 (1896). A. Joly, C. R., 97:456 (1883).	$\begin{cases} \text{B} + \text{C} \\ \text{Fe} + \text{B} + \text{C} \\ \text{Cu} + \text{B} + \text{C} \end{cases}$	black, brilliant cryst.	9.8	2.51
CoB	Moissan, C. R., 122:424 (1896); Ann. de Chim., 9:273-85 (1896).	$\text{Co} + \text{B}$	brilliant prisms several mms. long.	7+	7.25 at 18°
CrB	Moody & Tucker, J. Chem. Soc. Trans., (1902) p. 14-17.	$\text{Cr} + \text{B}$	gray, metallic.	8	5
FeB	Moissan, C. R., 120:173 (1895); Ann. de Chim., 9:273-85 (1896).	$\text{Fe} + \text{B}$	metallic crystals.		

MnB	B. du Jassonneix, C. R., 139:1209 (1904).	$\text{Mn}_3\text{O}_4 + \text{B}$ and treated by chlorine.	brilliant metallic powder.	6.2 at 15°
MnB ₂	Troost & Hautefeuille, C. R., 81:1263-6 (1875); Ann. de Chim., 9:65 (1876).	$\text{B}_2\text{O}_3 + \text{Mn}_3\text{C}$	violet gray crystals.	
Mo ₃ B ₄	H. R. Moody & S. A. Tucker, J. Ch. Soc. Trans. (1902) 14-17.	Mo+B	pale brass color, brittle.	7.1
NiB	Moissan, C. R., 122: 424 (1896); Ann. de Chim. 9: 273-85 (1896).	Ni+B	brilliant prisms several mms. long.	7.39 at 18°
Pt ₂ B	Martius, Annalen 109: 79 (1859); Descostils, Ann. de Chim. 67:88 (1808).	Si+B	brilliant black rhombic crystals, yellow if thin	2.52
SiB ₃	Moissan & Stock, C. R., 131: 139-43 (1900); Ann. de Chim. 20: 433 (1900).	Si+B	thick, black cryst.	2.47
SiB ₆	Moissan & Stock, C. R., 131: 139-43 (1900); Ann. de Chim. 20: 433 (1900).	$\text{B}_2\text{O}_3 + \text{SrO} + \text{Al} + \text{C}$	black crystalline powder.	3.28 at 15°
SrB ₆	Moissan & Williams, C. R., 125: 629-34 (1897); Bull. Soc. Chim., 17: 1015 (1897)	$\text{ThO}_2 + \text{B}$	yellowish metallic powder*	7.5 at 15°
ThB ₄	B. du Jassonneix, C. R., 141: 191-3 (1905)	$\text{ThO}_3 + \text{B}$	reddish violet powder	6.4 at 15°
ThB ₆	B. du Jassonneix, C. R., 141: 191-3 (1905)	W+B	silvery, metallic.	
WB ₂	Moody & Tucker, (see CrB)	Zr+B		
Zr ₃ B ₄	Moody & Tucker, E. Wedekind, Ber., 35: 3929-32 (1902).			
BaSi ₂	Disc. by C. B. Jacobs, July, 1899. Chem. News, 82: 149 (1900).	$\text{Si} + \text{CaCl}_2 + \text{Na}$		
CaSi ₂	Disc. by Wöhler, Ann. de Chim. 69: 224 (1863); Ann., 127: 255 (1863). G de Chalmot, Amer. Chem. J., 18: 319 (1896).	$\text{CaO} + \text{SiO}_2 + \text{C}$		
	C. B. Jacobs, British Assoc. (1900) p. 649. *Moissan & Dilthey, C. R., 134: 503-7 (1902); Ann de Chim., 26: 289 (1902); Bull. Soc. Chim., 27: 1199 (1902).	$\text{CaCO}_3 + \text{SiO}_2 + \text{C}$ $\text{Si} + \text{CaO}$	gray, brilliant cryst.	2.5
CSi	Schutzenberger, C. R., 114: 1089-93 (1892).	$\text{SiO}_2 + \text{C}$ $\text{Si} + \text{C}$ $\text{Fe}_2\text{Si} + \text{C}$ $\text{Fe} + \text{SiO}_2 + \text{C}$	colorless hexagonal crystals.	3.12
	Discov. E. G. Acheson, 1890. Moissan, Ann. de Chim., 9: 296-300 (1896).			

TABLE II—Continued.

	Literature and Discovery.	How Made.	Description.	Hard- ness.	Specific Gravity.
Ce_2Si_3	Ullik, Chem. Central., 1865 p. 1045	Electrolysis of $3\text{KF} \cdot 2\text{CeF}_4$ $\text{CeO}_2 + \text{Si}$	lamellar steel gray cryst. brittle.		5.67 at 17°
CeSi_2	*J. Sterba, C. R., 135:170 (1902); Ann. de Chim., 2:229-32 (1904).	$\text{Cu} + \text{Al} + (\text{Cr}_2\text{O}_3 \text{ in}$ silicate crucible	gray arborescent cryst. powder.	6+	6.52 at 18°
Cr_3Si	Zettel, C. R., 126:833-5 (1898).	$\text{Cr} + \text{Si}$	metallic cryst.	9+	
Cr_2Si	Moissan, C. R., 121:621 6 (1895); Ann. de Chim., 9:289 (1896)	$\text{Cr}_2\text{O}_3 + \text{SiO}_2 + \text{C}$	brilliant prisms.	6+	5.6 at 0°
Cr_3Si_2	*Lebeau and J. Figueras, C. R., 136: 1329-31 (1903).	$\text{Cu} + \text{Cr} + \text{Si}$			
CrSi_2	G. de Chalmot, Amer. Chem. J., 19:69 (1897).	$\text{Cr}_2\text{O}_3 + \text{SiO}_2 + \text{C}$	gray metallic needles.		4.39
Cr_2AlSi_3	W. Manchoth & A. Kieser, Ann., 337:353- 61 (1904).	$\text{Cr} + \text{K}_2\text{SiF}_6 + \text{Al}$		5	4.7
Cr_2AlSi_4	W. Manchoth & A. Kieser, Ann., 337:353- 61 (1904).	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{SiF}_6$ + Al		5+	4.8
Co_2Si	Vigouroux, C. R., 121:686-8 (1897); Ann. de Chim., 12:175 (1897).	$\text{Co} + \text{Si}$	steel gray cryst.		7.1 at 17°
CoSi	Lebeau, C. R., 132:556 (1901); C. R., 135: 475-7 (1902); Ann. de Chim., 27:271-7 (1902).	$\text{Cu}_2\text{Si} + \text{Co}$	brilliant prisms and oc- tahedra.		6.3 at 20°
CoSi_2 Cu_2Si	*Lebeau, Ann. de Chim. 27:271-7 (1902) Vigouroux, Ann. de Chim., 12:184 (1895); C. R., 122:318-19 (1896).	$(\text{Cu}_2\text{Si} + \text{Co} + \text{Si}$ $\text{Cu} + \text{Si}$	dark bluish cryst. steel gray, brittle crys- tals; reddens in air.	4.5 very hard	5.3 at 0° 6.9 at 18°
Cu_4Si	G. de Chalmot, Am. Chem. J., 19:118 (1897).	$\text{Cu} + \text{Si}$	silver white; reddens in air.	hard	7.48 at 0°
Fe_2Si	E. Vigouroux, C. R., 142:87-8 (1906). Disc. by Hahn, Ann., 129:57-76 (1864).	$\text{Si} + \text{Na} + \text{NaCl} +$ $\text{FeCl}_2 + \text{CaF}_2$	feebly magnetic		6.61 at 23°

Fe_2Si_2	Moissan, C. R., 121:621-6 (1895); Ann. de Chim., 9:289 (1896). *Lebeau, Ann. de Chim., 26:5-31 (1902). G. de Chalmot, J. Amer. Chem. Soc., 17:923 (1895). Encyclopaedie Freymy, Vol. 20, p. 93.	$\text{Fe} + \text{Si}$ $\text{Fe}_2\text{O}_3 + \text{Si}$ $\text{Fe} + \text{Si}$ $\text{Fe} + \text{SiO}_2 + \text{C}$	small metallic magnetic prisms. brilliant gray octahedra. brittle white cryst. feebly magnetic.	6 + very hard	6.85 at 20° 6.36
FeSi	Lebeau, C. R., 26:5-31 (1902). Disc. by Hahn, Ann., 129:57-76 (1864). G. de Chalmot, Am. Chem. J., 19:122 (1897).	$\text{SiCl}_4 + \text{Fe}$ $\text{Fe} + \text{Cu}_2\text{Si}$	metallic tetrahedric cryst	7 +	6.17 at 15°
FeSi_2	*Lebeau, Ann. de Chim., 26:5-31 (1902). Moissan, C. R., 134:1083-7 (1902); Bull. Soc. Chim., 27:1203-7 (1902). Wöhler, Ann., 107:119 (1858); Wöhler, Ann. de Chim., 54:218-25 (1858); Geuther, J. f. pract. Chem., 95:424; Phipson, Proc. Roy. Soc., 13:217 (1864). Brunner, Fogg. Ann., 101:264 (1857); Wöhler, Ann., 106: (1858). Vigouroux, C.R., 121:771-3 (1895).	$\text{Fe} + \text{Si}$ $\text{Li} + \text{Si}$	brilliant cryst brilliant indigo blue cryst very hygroscopic.	4 +	5.40 at 15° 1.12
Li_2Si_2		$\text{Mn} + \text{Si}$ $\text{Mn}_2\text{O}_4 + \text{SiO}_2 + \text{C}$ $\text{Mn}_3\text{O}_4 + \text{Si} + \text{H}_2$ $\text{Mn} + \text{Cu} + \text{Si}$	gray metallic crystals, brittle.		6.6 at 15°
MnSi	*Lebeau, C. R., 136:89-92; 231-6 (1903). Carnot & Goutal, Ann. des Mines, 18:27 (1900); H. N. Warren, Chem. News, 78:319 (1898). *Lebeau, C.R., 136:89-92 (1903). G. de Chalmot, Am. Chem. J., 18:536 (1895).	$\text{Mn} + \text{Cu} + \text{Si}$ $\text{Mn}_2\text{O}_4 + \text{SiO}_2 + \text{CaO} + \text{C}$ $\text{Mn} + \text{Cu} + \text{Si}$	brilliant prisms.		6.2 at 15°
MnSi_2	*Lebeau, C. R., 136:231-3 (1903). H. N. Warren, Chem. News, 78:318 (1898). *Vigouroux, C. R., 129:1238-9 (1899). Vigouroux, C. R., 121:686-8 (1895). Disc. by Guyard, Bull. Soc. Chim., 25:510 (1876); *Vigouroux, C. R., 123:117 (1896); Ann. de Chim., 12:188 (1897).	$\text{Mn} + \text{Cu} + \text{Si}$ $\text{Mn}_2\text{O}_4 + \text{SiO}_2 + \text{CaO} + \text{C}$ $\text{Mn} + \text{Cu} + \text{Si}$ $\text{MoO}_3 + \text{Si}$ $\text{Ni} + \text{Si}$ $\text{Pt} + \text{Si}$ $\text{Pt} + \text{Si}$	brilliant tetrahedric crystals. small dark gray octahedra. silver white prisms. steel gray crystals.	8-9	5.9 at 15° 5.24 at 13° 7.2 at 17° 13.8 at 15°
Mo_2Si_3					
Ni_2Si					
Pt_2Si					

TABLE II.—Continued.

	Literature and Discovery.	How Made.	Description.	Hard- ness.	Specific Gravity.
RuSi	Moissan and Manchot, C. R., 137:229-32 (1903); Ann. de Chim., 2:285 (1904) Bull. Soc. Chim., p. 559 (1904). See BaSi ₂	Ru+Si	metallic white prisms	very hard.	5.40 at 4°
SrSi ₂ Ti ₂ Si	L. Levy, C. R., 110:1368 (1890); 121:1148 (1895).	SrCO ₃ +SiO ₂ +C TiCl ₃ +Si	bluish white	hard.	
W ₂ Si ₃	Vignoroux, C. R., 127:393 (1898); Moissan C. R., 123:13 (1896); Warren, Chem. News, 78:318 (1898).	WO ₃ +Si	steel gray metallic crystals.		10.9
V ₂ Si	Moissan & Holt, C. R., 135:493-7 (1902); Ann. de Chim., 27:277-88 (1902).	VC+Si V ₂ O ₃ +Cu+Si	silver white prisms		5.48 at 17°
VSi ₂	Moissan & Holt, C. R., 135:493-7 (1902); Ann. de Chim., 27:277-88 (1902).	V ₂ O ₃ +Si	brilliant metallic prisms		4.42
Zr Si _x	E. Wedekind, Ber., 35:39:29 (1902).	ZrO ₂ +Si	dark crystals.		

The numbers denoting hardness in the above table are according to Mohr's scale; -6, orthoclase; 7, quartz; 8, topaz; 9, corundum; 10, diamond.

* In case of several articles upon the same compound, that marked by the asterisk is the more comprehensive.

Additional references are as follows:

- A summary concerning silicon and silicides to the year 1897, Vigouroux, *Ann. de Chim.*, 12: 5-71; 153-197.
- The preparation and properties of amorphous silicon, Vigouroux, *C. R.*, 120: pp. 94, 367, 554, 1161, 1393 (1895).
- New properties of amorphous silicon, Moissan, *Bull. Soc. Chim.*, 27: 1198 (1902).
- Silicon by electrolysis, Gore, 1884, *Chem. News*, 50: 113-4; Hampe, 1889, *Chem. Zeitung*, 12: 841; Minet, 1891, *C. R.*, 112: 1215-18.
- Controversy concerning the existence of a silicide of silver, H. N. Warren, *Chem. News*, 67: 303-4 (1893); Moissan, *C. R.*, 121: 621-6 (1895); G. de Chalmot, *Am. Chem. J.*, 18: 95 (1896); Moissan, *Ann. de Chim.*, 9: 294 (1896).
- The preparation of amorphous boron, Moissan, *C. R.*, 114: 392-7 (1892), *Ann. de Chim.*, 6: 296-320 (1895).
- Mulhauser (*Chem. Zeitung*, 26: 807) claims the discovery of silicon carbide for E. H. and A. H. Cowles, in 1884.

Unless there is other experimental evidence than that adduced in the original publication, it seems to the writer that the formulae given by H. R. Moody and S. A. Tucker for the "borides" of chromium, molybdenum, tungsten and zirconium, should be accepted by the chemical world with more than the proverbial "grain of salt." The only experimental evidence given for these formulae is as follows:

- CrB. "10 g. chromium and 2.1 g. boron were heated in the electric furnace for six minutes by a current of 175 amperes at 60 volts. The product contained 82% chromium, hence it is a definite chromium boride of the formula CrB." It should be noted that the charge contained originally 82.6% chromium.
- Mo₃B₄. "6 g. molybdenum and 1 g. boron were heated twenty minutes by 230 amperes at 70 volts. Analysis showed 86% molybdenum, hence the formula." This charge contained 85.7% molybdenum.
- WB₂. "4 g. tungsten and 0.2 g. boron, after five minutes heating by 175 amperes at 65 volts showed 89% tungsten, therefore the formula is WB₂." The charge contained 88.9% tungsten.
- Zr₃B₄. "15 g. zirconium and 2.2 g. boron were heated by 200 amperes at 65 volts for five minutes. Analysis showed 86% zirconium." The charge contained 87.2% zirconium.

It is probable that these four metals are capable of forming compounds with boron in definite proportions. It is possible that the formulae assigned are the correct ones for such compounds,—but these experiments *prove* nothing of the sort. From the energy and time of heating, the temperatures were very moderate, even low, for the electric furnace. Under these conditions all the elements concerned are only slightly, if at all, vaporized, so that the experiments consisted, in each case, in heating together two non-volatile elements in pre-determined proportions, and finding them in the same proportions in a homogeneous ingot after cooling. The only deduction from this is, that the two elements concerned are capable of alloying in the proportions originally taken. This is an excellent field for further investigation. E. Wedekind¹⁰ has obtained compounds of zirconium with boron, and with both boron and carbon by reduction of zirconium oxide by boron, but has not as yet been able to purify them or to assign a formula to either. It is the opinion of the writer that definite borides and silicides of iridium, osmium, uranium, and many of the metals of the rare earths, can be isolated, although these are as yet unknown.

In the following table (Table III), compiled from the original literature, the vigor of chemical action of reagents upon the borides and the silicides is indicated as follows:

N = no action.

S = slight action.

SS = very slight action.

R = acts readily.

V = acts vigorously.

VV = acts violently.

VVV = acts with incandescence.

Numerals indicate the approximate temperature in degrees centigrade.

¹⁰ Ber., 35: 3929-32 (1903).

TABLE III.—*Chemical Properties of the Borides and Silicides.*

Reagents	H ₂ SO ₄	HNO ₃	HCl	HF	HCl+HNO ₃	KOHsol.	Fused KOH	Fused K ₂ CO ₃	Fused Na ₂ CO ₃ +KNO ₃	Oxygen	Chlorine	HCl gas	Fluorine	H ⁺
Al ₂ B ₄ ...	...	R	SS	...	...	SS	VVV	...	...	...	VV at 800°	...	...	...
Al ₂ B ₂ ...	SS	R	N	...	...	...	...	...	...	...	...	...	...	...
Al ₃ B ₄ C ₂	SS	V	SS	...	...	N	...	...	...	...	...	...	...	...
BaB ₆ ...	N-dil. S-conc.	VV	N	...	...	...	...	...	...	N-20 SS-800	V-800°	...	VVV 20°	N 250
Be ₂ B ₆ C ₄	R	R	R	R	...	...	...	...	...	...	VVV 450	...	...	...
CaB ₆ ...	N-dil. S-conc.	VV	N	...	...	...	...	...	...	...	V-800	...	VVV-20	N 250
CB...	N	N	N	N	N	N	R	R	...	...	...	...	...	N
CB ₆ ...	N	N	N	N	N	N	V	V	...	N-500 V-1000	...	...	...	N
CoB...	N-dil. S-conc.	V	SSS	...	VV	...	VVV	VVV	V	VVV 800	VVV 800	...	...	S
CrB	S	S	S	...	S	...	V	V	...	VVV 800	V 800	...	...	N
FeB...	N-cold S-hot	V	SS	N	V	...	V	V	...	VVV 800	V 800	...	VVV-20	S
MnB...	V	V	R	V	...	S	VV	VV	...	R 700	V 800	...	...	S
MnB ₂	R	R	R	R	...	R	...	...	...	...	...	...	...	N
Mo ₃ B ₄	S	S	S	...	V	...	...	...	...	...	...	...	...	N
NiB...	N-dil S-hot	V	SSS	...	VV	...	VVV	VVV	V	VVV 800	VVV 800	...	VVV 20	S
Pt ₃ B...	...	...	...	N	...	...	R	V	V	...	VVV 800	...	VVV 100?	...
SiB ₃	S-hot	S	N	N	...	...	...	...	...	...	VVV 800	...	...	...

TABLE III.—Continued.

	H_2SO_4	HNO_3	HCl	HF	$HCl+HNO_3$	KOH-sol.	Fused KOH	Fused K_2CO_3	Fused $Na_2CO_3+KNO_3$	Oxygen	Chlorine	HCl gas	Fluorine	H_2O
SiB_6	S-hot	R	N	N			S	V	V		VVV 800		VVV 100	
SrB_6	N dil.	VV	N								V 800		N 20	
.....	S conc.												VV hot	
ThB_4	N-cold	V	V-hot			N	VVV			S 800	V 500	R 500	VVV warm	
ThB_6	N	R	N	N		N	VVV			S 800	V 500	R 500	VVV warm	
WB_2	S	S	S		V							R 500		
Zr_3B_3	S	S	S		S									N
$BaSi_2$		R	R	R	R					S				N
$CaSi_2$		SS	R	VV		R				SS 900	VVV 800		VVV 20	R
.....	R dil.		S 20			N dil.				SS	N 20			SSS
$CeSi_2$	V conc.	R	R 100	V		R-conc.	VVV			SS	VVV 800		V 20	SSS
Cr_3Si	N	N	N	R	N		S		V		VVV 800			
Cr_2Si	N	N	N	S-20					R		VVV 800			
Cr_3Si_2	N	N	S-conc.	V				V		SS 1100	R 700			
.....		N	100								R 400	R		N
$CrSi_2$			N-20	R	N-20				R					
Cr_2AlSi_3	N	SS	N	R	N	N	R			S 800	R 800			
Co_2Si	SS	SS	N	R	N	N	VV	R	V	S 1200	VVV 800	R 800	VVV 20	
$CoSi$	N	N	R		S	SS	VV			S 1200	V 300	R 700	VVV-warm	
$CoSi_2$	N	N	SS	V		S	VV			SSS 1200	V 300		VVV-warm	
Cu_2Si	R	V	R	S				R	R	N cold				
Cu_4Si	S	V	S	SS	S	S				S 800				
Fe_2Si	N	N	V	R	R	S			R					

In general, the borides and the silicides are brittle, metallic, harder than the corresponding carbides, and very resistant to chemical reagents. As seen from Table II, the usual method of preparing these compounds has been that of direct synthesis from the elements; occasionally the metallic oxide has been reduced by boron or silicon, and still more rarely, the oxygen compounds of both the metal and the non-metal have been simultaneously reduced by carbon or magnesium.

II.

REDUCING AGENTS.

This investigation requires a survey of the field of possible reducing agents, their properties, advantages, and limitations.

CARBON.

Carbon constitutes the most important reducing agent in technical metallurgy, and it has certain advantages over other substances for reduction in the electric furnace. It is cheap, it is a powerful reducing agent at high temperatures, so slightly volatile that it remains in the furnace, while the product of its action is a gas, and hence escapes as soon as formed. This last is an important advantage of carbon over most other reducing agents, which usually leave in the furnace slags that are hard to break up and difficult to get rid of by chemical means.

The great disadvantage of carbon is its tendency to form carbides with nearly all metals which are produced in the electric furnace, and also in the presence of silica or borax, to form the carbides of silicon and boron, extremely resistant to chemical reagents and difficult to remove from the product desired. In the reduction of the metallic oxides, the amount of carbon in the product may be made very small, and even negligible in some cases, by using an excess of metallic oxide in

the charge. In the preparation of borides and silicides from their oxygen compounds, however, this method of removal of carbon from the product is not available. If carbon, boric anhydride, and any metallic oxide are mixed in the proportions necessary for complete reduction, and then an excess of the metallic oxide be added for the purpose of removing carbon from the alloy or chemical compound which is desired, after reaction has occurred the unreduced substance will be, not the excess of metallic oxide, but its equivalent, as regards oxygen, of boric anhydride. Unlike the metallic oxide, this will have little, if any, effect in removing from the product any carbon which may have been taken up during the reduction.

Hence it will be seen that carbon is not a suitable reducing agent for use in the preparation of borides and silicides by the method proposed in this investigation.

SODIUM AND POTASSIUM.

Sodium and potassium, so often employed by chemists for difficult reductions, cannot be used at the high temperature of the arc furnace because of their violent action and volatility.

ALUMINUM.

The use of aluminum as a reducing agent began about the middle of the last century, but has assumed practical importance only within the last six years. The usefulness of carbon as a reducing agent is limited to the reduction of oxides, except that it removes the oxygen from ternary compounds such as the sulphates. Aluminum, however, is an effective reducing agent for sulphides and chlorides, as well as oxides.

The following outline shows in part the development of its use as a reducing agent.

1858. Deville and Wöhler¹¹ reduced boron trioxide by aluminum.

¹¹ *Ann. de Chim.*, 52: 63 (1858).

1858. Wöhler¹² formed a chromium-aluminum alloy from chromic chloride.

1859. Beketoff¹³ produced a 33% barium-aluminum alloy from barium chloride and barium oxide.

1860. Michel¹⁴ made aluminum alloys with manganese, iron, nickel, and titanium from their chlorides, also of tungsten and molybdenum from a mixture of chloride and oxide.

1861. Tissier¹⁵ introduced silver sulphide into fused aluminum and reduced it, but failed to reduce the sulphides of zinc, iron and copper!

1888. Beketoff¹⁶ obtained potassium and rubidium from their hydroxides by aluminum, but found that sodium and potassium separated aluminum from its chloride:

1888. L. Levy¹⁷ made an alloy of titanium and aluminum.

1893. Greene and Wahl* produced manganese on a commercial scale by heating a mixture of manganese oxide and granulated aluminum.

1895. Vigouroux¹⁸ reduced silica by powered aluminum.

1896. Moissan¹⁹ by introducing a mixture of metallic oxide and aluminum filings into a bath of fused aluminum, made alloys of aluminum with molybdenum, nickel, titanium, tungsten and uranium. He made a chromium-copper alloy by adding a chromium-aluminum alloy to copper, and then removed the aluminum by copper oxide.

1896. Combes²⁰ substituted a metallic sulphide or chloride for the oxide of Moissan's method in order to secure a better separation of the alloy from the slag.

1898. Goldschmidt²¹ heated in a crucible, mixtures of granulated aluminum with metallic oxides, chlorides and sulphides,

¹² Ann., 106: 118.

¹³ Ann., 110: 374.

¹⁴ Ann., 113: 248; 115: 102.

¹⁵ C. R., 52: 931.

¹⁶ Ber., 21: 424.

¹⁷ C. R. 106: 66.

* J. Frank. Inst, 135: 218-23.

¹⁸ C. R., 120: 1161-4.

¹⁹ C. R., 122: 1302-3.

²⁰ C. R. 122: 1482-4.

²¹ Ann., 301: 19-28, J. Soc. Ch. Ind., 17: 543-5.

producing a metal free from carbon and aluminum. In this way he reduced the sulphides of cobalt, lead, molybdenum, nickel and zinc, and stated that all sulphides could be reduced by aluminum except those of barium, calcium, lithium, magnesium, potassium, sodium and strontium (cf. Tissier above). He next turned his attention to the reduction of the oxides, from which he separated either in the pure state, or as alloys of aluminum, the elements boron, calcium, cerium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, niobium, potassium, sodium, tantalum, thorium, tin, titanium, tungsten, vanadium and zirconium, but found that aluminum would not reduce magnesia. He then developed his now well-known method of igniting the charge from the top by means of a cartridge of barium peroxide and aluminum, fired by magnesium ribbon.

1898. Franck²² reduced phosphates, with the formation of aluminum phosphide (Al_5P_3) and the liberation of phosphorus, and reduced the carbonates of barium, calcium, lithium, potassium, sodium, and strontium by heating with pulverized aluminum. The metal liberated alloyed with excess of the reducing agent. He remarked that the oxides of copper, lead and silver were reduced explosively, and that the presence of calcium sulphate in calcium phosphate caused explosive reduction. Goldschmidt had called attention to explosions caused by sulphates, in reducing ferric oxide and molybdenum oxide.

1901. Duboin²³ reduced the alkaline earths by ignition with powdered aluminum or magnesium in hydrogen.

1903. Rossi²⁴ reduced ores of titanium and tungsten in ton lots, by melting aluminum in the electric furnace, and then feeding in the ore. The product contained only traces of aluminum and carbon.

1904. Goldschmidt²⁵ gave an account of his production of

²² Chem. Zeitung, 22:236-45, J. Soc. Ch. Ind., 17:612.

²³ C. R., 132: 826-8.

²⁴ Electrochem. Ind., 1: 523.

²⁵ Electrochem. Ind., 2: 145-7.

carbon-free metals and alloys. In 1902, Dr. Goldschmidt had succeeded in obtaining, by his process of firing a charge of the oxide and pulverized aluminum, only the following metals in a solid, coherent mass: chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, niobium, tantalum, and tin. Later the niobium was found by Muthmann to contain aluminum. Silica and vanadic acid were not reduced, while barium, beryllium, boron, cerium, thorium, titanium, tungsten, and uranium were scattered throughout the slag. Alloys of these metals have been produced, however, by adding to the charge some easily reducible oxide like that of iron, to supply heat enough to secure fusion and a complete reduction.

1905. W. Huppertz²⁶ in attempts to reduce titanium oxide by the Goldschmidt process, in order to bring about complete reaction, combined electric heating with the aluminothermic method. With certain precautions, he believes that it will be possible in this way to produce pure titanium in large masses from rutile.

As indicated above, aluminum as a reducing agent has received much attention from scientific investigators, and has proved very efficient. Aside from its high price, it has two disadvantages; one will be mentioned under slags; the other is its remarkable tendency to form alloys. In respect to the number of metals with which it will unite, it equals, if it does not exceed, carbon. When it is used in ingots for the reduction of metallic oxides, an alloy of aluminum is usually produced. Goldschmidt has overcome this difficulty by using aluminum in the form of powder or grains. There are, however, as mentioned, certain oxides from which only alloys can be obtained by this method.

Early in the course of this investigation, entirely independently of the work of Huppertz, the writer developed a method of firing in the electric furnace a charge consisting of powdered aluminum and any other powdered substance or substances that he desired to reduce, and obtained a product free both from

²⁶ Abstract in *Electrochem. Ind.*, 3:35, of articles in Nos. 17-22 *Metallurgie*.

carbon and aluminum. Besides applying the method to rutile, as was done by Huppertz, titanite, boric and tungstic "acids" were similarly reduced, and by the addition of a retarder, to check the vigor of reaction, ordinary Goldschmidt charges were fired in the electric furnace without accident. The first such experiment was made in December, 1904, from which time the method was regularly used. In all about fifty reductions were made by powdered aluminum in the electric furnace.

CALCIUM CARBIDE.

Like aluminum, calcium carbide is a convenient medium for the storage in concentrated form of energy derived from steam or water power, so that it can be conveniently transported and applied in a small space.

H. N. Warren²⁷ appears to have first suggested the use of calcium carbide as a reducing agent, stating that the oxides of chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, tin, and tungsten yield calcium alloys when heated with calcium carbide.

Moissan²⁸ reduced metallic oxides by calcium carbide in the electric furnace, and obtained the carbides Al_4C_3 , Cr_3C_2 , Mn_3C , Mo_2C , SiC , TiC , and W_2C . With the easily reducible oxides of copper and lead, he found reaction to occur before the charge was heated to fusion. The equation of reaction for lead oxide is



The reduced metal contained no calcium, contrary to the results of Warren's experiments. Reduced bismuth and copper were also free from calcium. In the course of Moissan's article, he said that he had previously²⁹ indicated that calcium carbide is a strong reducing agent. This statement, however, is not borne out by the article referred to, in which no mention

²⁷ Chem. News, 75: 2, Jan. 1st (1897).

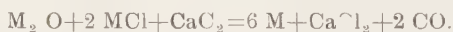
²⁸ C. R., 125: 839-44 (1897); Bull. Soc. Chim., III, 19: 870 (1897).

²⁹ C. R., 118: 501 (1894).

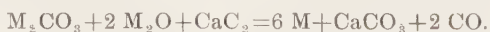
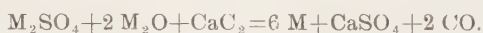
is made of calcium carbide as a reducing agent. The only experiments which might be construed to bear upon its reducing properties, are heating it with some powerful oxidizing agents. With fused "chromic acid," calcium carbide became incandescent. Potassium chlorate and nitrate at their melting points had no sensible action upon it, but at a red heat, they produced incandescence. Lead peroxide with calcium carbide became incandescent at a dull red heat. These experiments were described, but with no deductions as to the reducing character of calcium carbide.

Tarugi³⁰ confirmed Warren's formation of calcium alloys by the reduction of the oxides of copper and lead, and stated that all salts of antimony, bismuth, cadmium, cobalt, gold, nickel, platinum, silver, tin, and zinc, when heated with calcium carbide, yielded alloys (cf. Warren) readily decomposable by water. He reduced the oxide, phosphate, chloride, sulphate, carbonate, and borate of copper.

B. Neumann³¹ reduced metallic oxides, chlorides, carbonates, and mixtures of these, with calcium carbide by heating the charges in clay crucibles in a furnace. He found that chlorides are most easily reduced, and gave the following equations:



With sodium chloride as flux, copper, lead and nickel are obtained in mass while some metals are scattered in globules, and others vaporize.



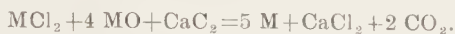
In a brief article³² Fr. von Kügelgen stated that carbon dioxide is formed in these reactions instead of carbon monoxide, and supported this contention in a long article.³³ He gave as the equation of reaction:

³⁰ *Gazetta chim. ital.*, 29, i, 509-512; Abstract in *Chem. Zeit.*, 23: 292 (1899); Abstract in *Zeit. f. Electrochem.*, 7: 542 (1899).

³¹ *Chem. Zeitung*, 24: 1013-4.

³² *Chem. Zeit.*, 24: 1060 (1900).

³³ *Zeit fur Electrochem.*, 7: 441-50; 557: 573 (1901).



In addition to a long series of metallic oxides, chlorides, and mixtures of these (among them sodium chloride and magnesium chloride), he reduced sodium and potassium hydroxides by calcium carbide. Magnesium oxide is not reduced, but alumina is partially reduced. Mixtures of carbide with the following may be kindled by a match: zinc chloride, copper chloride, copper oxide, silver chloride, tin chloride, bismuth chloride, chromium chloride.

This difference of opinion in regard to the formation of carbon monoxide or carbon dioxide in the reduction resulted in a lengthy controversy between Neumann³⁴ and Kügelgen.³⁵ The facts appear to be that with easily reducible compounds, the product is mainly, and in some cases entirely, carbon dioxide; at the higher initial temperatures required by compounds which are reduced with greater difficulty, increasing amounts of carbon monoxide appear as a product.

Geelmuyden³⁶ used calcium carbide as a reducing agent in the electric furnace. He reduced boric anhydride with the production of calcium boride, and also reduced the sulphides of antimony, iron, lead and magnesium. The metals vaporized with the exception of iron; this was contaminated by carbon. Aluminum sulphide was not reduced by calcium carbide.

Calcium carbide, then, reduces the same classes of compounds as are reduced by aluminum and is especially advantageous to use for mixtures of an oxide with a chloride or a sulphide. It seems to be settled that calcium alloys are produced in certain reductions, but the exact conditions which cause their formation are not yet established. The products are contaminated by carbon under the same conditions, and possibly to the same extent, as if free carbon were used for reduction.

³⁴ Chem. Zeitung, 24: 1013-14; 26: 176, 1108 (1902); 27: 1026-8 (1903).

³⁴ Chem. Zeitung, 24: 1013-14; 26: 176, 1108 (1902); 27: 1026-8 (1903). Zeit. f. Electrochem., 8: 772-5; 795; 939 (1902); 9: 699-701 (1903).

³⁵ Chem. Zeitung, 24: 1060 (1900); 27: 743 (1903). Zeit. f. Electrochem., 7: 541, 557, 573 (1901); 8: 781 (1902).

³⁶ C. R., 130: 1026-9 (1900).

ALUMINUM CARBIDE.

Aluminum carbide would seem especially advantageous for scientific purposes in the reduction of mixtures of oxide with chloride or sulphide.

SILICON CARBIDE.

B. Neumann³⁷ states that by using sodium carbonate as a flux, carborundum reduces metallic oxides. Carborundum has been tested by the writer in the preparation of silicides, for which use it has the advantage of serving at once as reducing agent and source of silicon. Similarly, boron carbide might be used to advantage for making borides, but so far as the writer knows, this has not yet been tried.

CALCIUM.³⁸

If we may rely upon the claims of several experimenters, the problem of the production of calcium has been solved, and we may soon expect to find it on the market at a price that will make it available for use on a large scale. Current prices are as follows:

London, April, 1905:

One pound bars	\$3 92
Five pound tins, per pound	\$2 32

New York, May, 1905:

One hundred grams	\$3 00
One pound	\$10 00

As a reducing agent, it may be regarded, like aluminum and calcium carbide, as merely a convenient medium for the

³⁷ Zeit. f. Electrochem., 8:772 (1902).

³⁸ K. Arndt, Zeit. f. Electrochem., 8:861 (1902). Borchers and Stockem, Zeit. f. Electrochem., 8:751-8; 938 (1902). Borchers and Stockem (translation), Elect. World and Engin., 40:1002. J. H. Goodwin, J. Amer. Chem. Soc., 25:873-6 (1903). J. H. Goodwin, Proc. Amer. Philosoph. Soc., Vol. 43: No. 178; Abstracted Electrochem. Ind., Feb. 1905: p. 80-81.

storage, transportation, and application of the energy of water power or that derived from coal. Where purity of the product of reduction is of importance, calcium would seem as a general reducing agent superior to any other. In the electric furnace it should reduce most, if not all, of the oxides, chlorides, and sulphides which we are now able to reduce by other agents. It contains no carbon to be introduced as an impurity into the product. In the reduction of oxides alone, the slag formed, lime, is easily fluxed by certain substances, and even if it should remain as calcium oxide in the furnace, its density, tenacity, hardness, and resistance to acids are all less than for alumina, and render it in these respects a much less objectionable substance to have in the furnace than the latter.

The metal in granular or powdered form, can undoubtedly be used as aluminum now is in the Goldschmidt method of reduction. For this use it will be superior to aluminum for difficult reductions. For one equivalent of oxygen, its heat of oxidation is ten per cent. greater than that of aluminum—a sufficient increase to insure the completion of certain reductions that by aluminum are only partial. Mixtures of oxides with calcium will undoubtedly have a considerably lower kindling point than those with aluminum, a quality which will be a convenience, and will tend to cause more rapid and complete reaction.

A disadvantage of calcium as compared with aluminum is its oxidation at ordinary temperatures. Another, and possibly serious objection to calcium as a reducing agent in the electric furnace, is to be seen in the strong oxidizing action of fused lime upon silicon, boron, chromium, cobalt, iron, manganese, nickel, and titanium in the experiments of Moissan.³⁹

In spite of these objections to the use of calcium as a reducing agent in the electric furnace, the writer regards it as the most promising of any agent yet suggested for difficult reductions.

³⁹ C. R., 134: 280 (1902).

“MISCHMETALL.”⁴⁰

The latest reducing agent for oxides is the “mischmetall” produced from the cerite minerals, and consisting of cerium forty-five per cent., lanthanum twenty per cent., didymium fifteen per cent., and the remainder of samarium, erbium, gadolinium, and yttrium. The advantages claimed for this over the other metallic reducing agents, are its low kindling point, 150°, and the ready fusibility of the oxides formed by its action, as compared with magnesia and alumina. Its low kindling point causes an exceedingly rapid reaction, and the fusible slag produced permits the reduced metal to collect to a regulus. By its use the following metals were obtained from their oxides in a state of the highest purity: cobalt, chromium, iron, manganese, molybdenum, niobium, tantalum, and vanadium. The oxides of lead, tin, titanium, and zirconium yielded only alloys. With silica the reaction is feeble. Tungstic acid is reduced but gives only a dark brown mass. The authors believe that by working with kilogram lots, a regulus of tungsten might be obtained.

III

SLAGS.

A matter of nearly as great importance as the reducing agent, is the nature of the slag formed by its action. Some of the effects of slags have already been mentioned. The following classification of the action of slags, while based on their action in an electric furnace of the arc type, will apply more or less to all high temperature work.

1. A fluid slag conduces to complete reaction; with a solid slag, reaction will be incomplete. This points to the selection of different reducing agents according to the maximum tem-

⁴⁰ L. Weiss and O. Aichel, *Ann.*, 337: 370-89 (1904). Abstract *J. Chem. Soc.*, 1905, p. 164.

perature attained—or at least permits the use at high temperatures of reducing agents which could not be used at lower temperatures. The success of the Goldschmidt method of reduction depends upon the attainment of a temperature at which the slag, alumina, is perfectly fluid. The substitution of a sulphide for part of the metallic oxide in the charge should help in the more difficult reductions by the Goldschmidt method on the core of a more fluid slag, since aluminum sulphide is more fusible than aluminum oxide.

2. The slag protects the metal or metallic compound which is dense enough to sink through it from the direct radiation of the arc, and yet if fluid, the slag conveys heat very rapidly to this metallic charge or product.

3. A considerable quantity of slag fixes at its own boiling point the maximum temperature to which the product is subjected.

4. The slag may exert a purifying or an injurious effect upon the product, according to its chemical nature.

5. By adding calculated amounts of metallic oxide to the slag, used as a protection, metals may be melted below the arc without contamination by the carbon which falls from the electrodes. This method of fusing carbon-free metals has been developed in the course of this investigation.

IV

ELECTRICAL EQUIPMENT.

SOURCE AND CONTROL OF THE CURRENT.

The dynamo which supplied current for most of the experiments was a direct current 110 volt machine, rated at 825 amperes. Alternating current with variable voltage was also available up to twenty kilo-watts, and was occasionally used.

The direct current most frequently used was controlled by an iron water-pipe rheostat of ten equal sections in series, hav-

ing a total resistance of 0.5 ohm. With all but one section of the rheostat short-circuited, 600 amperes was delivered at a pressure of 80 volts at the furnace terminals. Of the total energy transformed by the generator, the per cent. delivered to the furnace was as follows:

Average for an entire experiment.....	68 per cent.
During maximum load (600 amp. x 80 volts).....	73 per cent.
Highest per cent for ten consecutive minutes in any experiment.....	80 per cent.
Highest per cent ever attained, for two minutes, by running the furnace directly from the dynamo	94 per cent.

The furnace was started with the entire rheostat in the circuit, which explains the low average. In experimental work, the convenience of this method of control more than compensates for the waste of energy. This waste of energy might be considerably diminished by having some sections of the rheostat of one-half and one-third the resistance of the others, with a generator voltage of eighty or ninety instead of one hundred and ten.

It is stated by Mrs. Ayrton⁴¹ "without some external resistance, it is impossible to maintain a silent arc between solid carbons." From the behavior of the arc when the resistance of the rheostat was reduced to only 0.05 ohm, the writer believed that even this resistance might be dispensed with, and yet the arc would run steadily. This was verified by an experiment. The furnace was heated, as usual, with the line voltage at 110. The voltage regulator was then cut out, the voltage lowered to 70, and the last section of the rheostat short-circuited. The only resistance external to the arc was that of the cables and armature,—between 0.012 and 0.018 ohm. The arc ran satisfactorily, although not so steadily as with one section of the rheostat in the circuit. The voltage of the generator was then raised to 80 with the result that the widest variations of current for an arc $1\frac{7}{8}$ inches in length was from 310 to 450 amperes. It is probable that most of this variation

⁴¹ The Electric Arc, p. 250

was due to the defective form of the anode, developed during the preliminary heating. The average resistance of the arc was twelve times that of the remainder of the circuit, and consequently the per cent. of energy delivered to the furnace was 92 +.

In this experiment, it was observed that when the arc became silent after it had been "shrieking," the voltage across the terminals diminished and the current increased. This is contrary to Mrs. Ayrton's observation upon the open arc.⁴²

These differences between the action of the arc lamp and the arc furnace would undoubtedly yield interesting results if thoroughly investigated.

ELECTRIC FURNACES.

For the production of metallic borides and silicides by the direct reduction of oxygen compounds, the horizontal arc furnace was decided upon as most easily managed and best suited to the purpose.

Several different materials of construction were tried and rejected. Finally magnesite brick was decided upon as being by far the most resistant material available for the furnace. Other materials tried were limestone, ordinary fire brick, chromite, and silica brick. The only limestone obtainable was very easily broken, and as a furnace material cracked badly, even when protected from the arc by a graphite lining. It is quite possible that a harder, stronger limestone, and particularly a dolomite, might prove a satisfactory material for furnace construction. Ordinary fire brick cannot be used for the inner zone of an arc furnace because of its fusibility. Silica and chromite brick, while less fusible than fire brick, are still far from satisfactory. The former fuses and disintegrates by the heat of the arc, and the latter cracks badly before its fusing point is reached. Both are distinctly more fusible than magnesite brick, and are more readily attacked by slags.

In point of infusibility, magnesite bricks are very satisfac-

⁴² *The Electric Arc*, p. 279.

tory, being melted to a depth of less than $\frac{1}{4}$ inch by ten minutes exposure to an arc of 600 amperes at 80 volts only an inch below the brick. They do, however, crack under the influence of heat, and must be handled very carefully. These brick were obtained from the Harbieson-Walker Refractories Co.

In form, the furnaces consisted of a box built of magnesite brick without cement, surrounded by a second layer of fire brick. The dimensions of the horizontal arc furnace were: outside—20 inches square, 26 inches high; and inside— $8\frac{3}{4}$ inches long, 7 inches wide, 7 inches deep—429 cubic inches. The outside dimensions included the ventilated base of fire brick. Although the table on which the furnaces stood had a thick cement top, it was found necessary to have air circulation between the body of the furnace and the table top. The furnace is shown in Figure I.

The cover consisted of two magnesite bricks, and the electrodes entered through holes drilled in the bricks which formed the ends. Later, the ends were simply built up around the electrodes, and the cracks stuffed with asbestos paper. This type of furnace, with two modifications, was used in about one hundred and thirty experiments.

Much trouble was experienced from the contamination of the products by iron. Even after all materials that entered into the composition of the charges were rendered iron free, the iron was still found, and its source was finally discovered to be the magnesite brick. A fused metal resting upon these in the presence of a strongly reducing slag, will be contaminated by iron. To remedy this, a bed of powdered magnesia, free from iron, was spread an inch deep in the bottom of the cavity. This prevented any contamination from the bottom of the furnace, but there was still occasional contamination from the side walls. For a part of the work, the entire inside, except for the bottom and the upper half of each end, was lined with inch-thick sheet graphite. Although this introduced carbon, it effectually prevented contamination by iron, and greatly

prolonged the life of the magnesite brick. With the graphite lining, the inside dimensions were $8\frac{3}{4}$ inches by five inches by six inches—262 cubic inches.

It would have been an advantage if the bottom of the furnace had been laid in cement, or strapped with iron to prevent the bricks from separating with the alternate expansion and contraction.



FIGURE 1. —The Electric Furnace.

For the short duration of the heating, fifteen to twenty minutes, with a powerful current for less than half this time, the heat insulation was found to be ample. The outside layers of brick could be removed by the bare hands, if done as soon as the current was shut off, although an hour later, they might become red-hot. The nearer air-tight the furnace is, without actually being so, the better.

The electrodes used were of Acheson graphite. The maximum current permissible on account of oxidation of the electrodes outside of the furnace has been determined in the course

of this work to be as given in the following table for twenty minutes heating:

Table IV.

Diameter.	Amperes.
1 inch.	400+.
1 $\frac{1}{4}$ inch.	650+.
1 $\frac{1}{2}$ inch.	960.
2 inch.	1600.

The capacity of the first two sizes is from direct measurement; that of the last two is calculated from the areas of their sections, since the maximum current used, 700 amperes, never heated them to redness. If the heating is prolonged to an hour or more the current allowable is about fifteen per cent. less than in Table IV.

Although 600 amperes has been used for a short time with one inch electrodes, these become red their entire length, and undergo oxidation. It was found that this oxidation could be prevented by painting them with a paste of water glass and carborundum dust.

Moissan ("Le Four Electrique") has given the size of carbon electrodes suitable for furnaces of different horse-power. As he ordinarily used fifty or sixty volts, the latter value has been used in calculating the following table, except in one case where he specified seventy-five volts. The results as calculated from Moissan are given in Table V.

Table V.

Diameter.		Amperes.
m. m.	Inches.	
16-18	$\frac{1}{8}$	120
27	1	450
40	1 $\frac{1}{2}$	1,250 (100 H. P.)
50	2	3,700 (300 H. P.)

In this table the current densities per unit area increase greatly with increase of diameter, although from the fact that the radiating surface increases less rapidly than the cross section, the reverse would be expected. Either the capacity of

the smaller electrodes is greatly underrated, or that of the larger ones much overrated. The only carbon electrode tried by the writer was of one inch diameter, and this became red-hot outside the furnace at 150 amperes, although Moissan stated that he was able to use 450 amperes. It would be of interest to the worker with the electric furnace to know whether the relative conductivities of carbon and of graphite for heat are in the same ratio as their electrical conductivities, as is the case for the metals. If this is so, there will be no advantage of either over the other in regard to the amount of heat wasted by conduction from the furnace.

On account of their being such good conductors of heat, the graphite electrodes used should be the smallest that will carry the desired current. They should be slightly pointed before use, and set exactly in line in the furnace. The source of any irregularity in the operation of the arc is usually found in the anode, which corrodes irregularly, while the cathode keeps in good order without attention. One advantage of alternating over direct current for the arc furnace is that both electrodes tend to keep in good form.

V.

EXPERIMENTS.

After this detailed consideration of the subject of reducing agents, the general action of slags, and the construction and operation of the furnaces employed, attention may be directed to the problems proposed, viz., the production of borides and silicides from their oxygen compounds by a single reaction in the electric furnace, and the production, if possible, of certain silico-borides by the same means.

The experimental work, results of which are here given, covered a period extending from December, 1903, to May, 1905, and included 160 electric furnace runs, with associated

analytical work. Each run involved the preparation of the materials, the weighing and mixing of the charge, the partial or complete construction of the electric furnace before, and the dismantling after, a run, and required from one to seven hours, varying with the time needed to prepare the materials of the charge, and to construct the furnace.

In addition to this, there was the disintegration of the product by acids, always requiring a day or more, and in some cases involving the trial of a number of organic in addition to the mineral acids. When a crystalline residue remained, this was tested qualitatively, and if promising, was subjected to a quantitative analysis.

Several runs of the furnace were for the purpose of preparing materials needed, such as borax glass, and boric anhydride; others, although not described in detail, contributed to the results obtained; while there were many experiments which were of use only in showing what arrangement of furnace or what materials were to be avoided.

A most serious limitation upon the work was the difficulty of carrying on the analytical processes. The resulting products required the working out and application of new methods of analysis. Boron, especially, presented much difficulty in its determination, and the available methods for its determination, especially when combined with various metals, are at best only partially satisfactory approximations. In several of these analyses the writer is indebted to Mr. William Hoskins of Chicago for valuable assistance.

PRELIMINARY EXPERIMENTS.

Beginning in December, 1903, a series of experiments were undertaken in the preparation of silicon in the electric furnace. Silica, glass, and calcium and sodium silicates were used as the source of silicon, and the reducing agents were carbon, aluminum, and carborundum.

The following difficulties were noted in the reduction by carbon:

- a. The melting point, 1430°C ,⁴³ and the boiling point of silicon are evidently near together, and as the reduction temperature is high, much silicon was often vaporized.
- b. The specific gravity of silicon (2.34) is about the same as that of most of the silicate charges used (S. G. quartz 2.5), hence the silicon remained diffused in the slag in small spheres instead of settling to the bottom in a single mass.
- c. Because of its brittleness, the masses of silicon that were occasionally obtained were broken in removing them from the slag.

The best results were secured with a charge containing much sodium silicate, thus lowering the density of the fluid bath and permitting the silicon to sink in it. By this means, a bar of silicon six inches long, $1\frac{1}{4}$ inches wide, and $\frac{3}{4}$ inch thick was formed in the furnace, but was broken into three pieces in removing it from the slag.

Reduction by aluminum was easily accomplished by adding the metal in lumps, to any melted silicate of the alkali or alkali-earth metals, containing cryolite or fluor spar as a flux for the alumina formed. When the action was brief, the resulting lumps of metal on treatment by hydrochloric acid, left the silicon as a crystalline powder. By prolonged action, the product appeared to be massive silicon, but still contained a trace of aluminum.

Nineteen experiments were tried, mainly with some type of resistance furnace. A method frequently used was to cover the electrodes with fragments of the silicate, start the arc, and as soon as a fluid bath was formed to draw the electrodes apart and allow the melted silicate to serve as the resistor.

By these various methods, a few pounds of silicon were produced in globules and fragments. This afterward served as a source of silicon in some of the experiments which follow.

⁴³ F. J. Tone, in *Electrochem. Ind.*, 3:183 (1905).

SILICIDES.

The first effort in this field was an attempt to prepare a new silicide, that of phosphorus. Phosphorus unites with many metals to form compounds akin to the borides, carbides and silicides. Since compounds of silicon with both boron and carbon have been obtained, it seemed probable that phosphorus would also unite with silicon. Further encouragement was found in the existence of the following compounds: SiS_2 , SiSe_2 , BP , and B_5P_3 .

The first experiment consisted of the reduction by carbon of a mixture of phosphoric acid and silica. The charge was made according to the molecular proportions ($2\text{HPO}_3 + \text{SiO}_2 + 7\text{C}$) by dissolving glacial phosphoric acid in water, and stirring in finely pulverized silica and carbon. The mixture was dried, ignited, and then heated in an open graphite crucible in the electric furnace for four minutes at 500 amperes and 50 volts. A greenish-yellow flame was seen at first, but it quickly died out. The product looked like the original mixture, and gave no indication either of phosphorus or of a phosphide when treated with acids.

With the idea that fused copper or copper silicide would make a good solvent for the interaction of silicon and phosphorus, the following charge was prepared:

Glacial phosphoric acid.....	40 grams.
Carborundum.....	20 grams.
Silica.....	5 grams.
Copper.....	30 grams.
Aluminum.....	20 grams.

This mixture was heated in a covered graphite crucible for 13 minutes at 200 amperes and 60 volts. When the metallic product was treated with hydrochloric acid, a gas was evolved which burned with a greenish-yellow flame when kindled. The product appeared to be metallic phosphides only.

Slight variations of this experiment were tried, but with no better results.

Direct union of the two elements was next tried, with tin as a solvent. Red phosphorus was dissolved in melted tin, and a phosphor-tin produced, containing 7 per cent. phosphorus. This was heated with pulverized silicon by the blast lamp, but without effect upon the silicon. Then the electric furnace was used. All silicon had vanished, and the crystalline metal had a strong odor of phosphorus. Hydrochloric acid acted upon it readily, and the gas evolved, burned, when kindled, with a yellow flame and the formation of a white smoke. If any silicide of phosphorus had formed, it was destroyed in dissolving the tin.

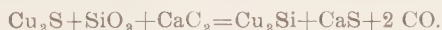
As the results of these experiments were not encouraging, the attempt to prepare a silicide of phosphorus in the electric furnace was abandoned.

Production of Silicides from Sulphide Ores.

The possibility of forming silicides by the simultaneous reduction of silica and a metallic sulphide was next investigated. The experiments were confined to such material as was immediately available and were directed to the formation of silicon-metals, not to the isolation of silicides of definite formulae.

Silicon-Copper from Chalcocite (Cu_2S .)

A charge was prepared consisting of 63.2 grams chalcocite, 24 grams ground quartz, and 35 grams calcium carbide, the proportions having been determined from the equation,



The calcium carbide was estimated as 80 per cent. pure.

The source of heat was a resistor of granular graphite upon which was placed the crucible containing the charge. This crucible was cut from a block of Acheson graphite, as it had been found by previous experiment that the ordinary "graphite crucibles" used for metallurgical operations, were destroyed in an electric furnace of this or the arc type. The heat record was:

Time.	Amperes.	Volts.	Resistance.	Per cent. of resistance at outset.
5:55	160	100	0.62 ohms	100
.....	200	98	.49 ohms	79+
5:59	340	92	.23 ohms	37+
6:00	500	83	.17 ohms	27+
6:01	550	80	.14 ohms	22.5

Although the charge had been intensely heated, no metal was found. It was reheated in a similar way for 17 minutes without effect. Lime as a flux and fresh materials were added, giving it the composition,

Sand.....	360 grams.
Chalcocite.....	379 grams.
Lime.....	324 grams.
Calcium carbide.....	35 grams.
Anthracite coal.....	120 grams.

This was heated half an hour at 300 amperes and 70 volts in a vertical furnace consisting of a box built of sheet graphite, 5 inches square and 6 inches deep. The charge served as one electrode. The result was an ingot of brittle white metal weighing 250 grams. By analysis, the composition was:

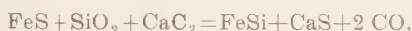
Copper.....	81.6 per cent.	
Iron.....	7.7 per cent.	Cu ₃ Si.....24.75 per cent.
Silicon.....	6.4 per cent.	or Fe ₃ Si..... 9.62 per cent.
Carbon.....	1.0 per cent.	Copper.....61.35 per cent.
Undetermined.....	3.3 per cent.	
100.0 per cent.		

As no sulphur was present, it is evident that the ratio of lime to sulphur used in this case, 4.2:1, was sufficient for its removal. The product contained 16 grams of silicon, or 10 per cent. of the total silicon in the charge. The yield was 53 per cent. of the combined weight of metal and silicon in the charge.

Ferro-silicon from ferrous sulphide.

In the first experiment, 560 grams of ferrous sulphide, 448 grams of lime, and an excess of glass were reduced by anthracite coal in the vertical furnace. The time of heating was 40 minutes by a current of 200 amperes at 50 volts. The product, a low grade of ferro-silicon, contained a small amount of sulphur. The ratio of lime to sulphur in this charge was 2.2:1, yet this is far above the theoretical ratio, 1.75:1. An explanation offered for the failure of the considerable excess of lime to remove all sulphur is that the lime entered into combination with the large excess of glass present, so that the usual stage of equilibrium between these weights of ferrous sulphide and lime was not attained.

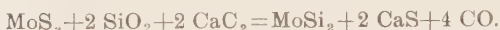
In a second experiment, ferrous sulphide was reduced in the horizontal arc furnace at a higher temperature. The charge was in accord with the equation,



with the addition of sodium chloride and cryolite as a flux. The heating was for 16 minutes at 450 amperes and 87 volts. The yield was 80 per cent. of the weight of metal and silicon only 53.3 per cent. of the combined weight of metal and silicon in the charge. Had the charge contained an amount of lime equivalent to the carbide, the ratio of lime to sulphur would have been 2.0:1; yet the product was free from sulphur. This tends to confirm the view that the glass was responsible for the presence of sulphur in the previous experiment.

Silicon-nickel from Millerite.

The charge of 107 grams NiS, 110 grams SiO₂, and 54 grams of powdered aluminum was heated in the horizontal arc furnace. Only a few globules of brittle, white metal, silicon-nickel, resulted. A fire brick had melted and flooded the interior of the furnace with slag. The experiment was not repeated.

Silicon-molybdenum from molybdenite.

The charge consisted of 48 grams molybdenite, 86 grams ground quartz, and 300 grams calcium carbide. The large excess of carbide was used in the hope that much of it would remain unchanged and yield a slag that could be decomposed by water. This charge was heated in the vertical furnace for 25 minutes by a current of 400 amperes and 70 volts. The result was an ingot of metallic lustre, white, brittle, and harder than quartz. Its weight was 32 grams. There was in the charge 28 grams of metal, 40 grams of silicon, and an excess of carbide over that required theoretically for complete reduction, so that the yield was only 47 per cent. of the theoretical amount. Water had but a very slight action on the slag, showing that the carbide was practically all destroyed. As expected, the slag evolved much hydrogen sulphide when treated with hydrochloric acid.

Other experiments were tried upon molybdenite using aluminum powder as a reducing agent, with similar results in regard to the nature of the product and the per cent. of yield.

Conclusions.

1. Metallic sulphides and silicates can be simultaneously reduced by calcium carbide or aluminum, with the production of a silicon alloy.
2. The total yield based on both the metal and non-metal in the charge is little above 50 per cent.
3. The use of carbon or a carbide as reducing agent introduces carbon into the metallic silicides of those metals capable of uniting with carbon.
4. The product can be obtained entirely free from sulphur by the use of lime or aluminum.

A NEW SILICIDE OF MOLYBDENUM.

The only silicide of molybdenum heretofore known is that discovered by Vigouroux in 1899, having the formula Mo_2Si_3 . In one of the attempts to prepare a silico-boride of molybdenum, the writer believes he has demonstrated the existence of a higher silicide.

The charge consisted of 70 grams molybdic acid, 30 grams silica, 50 grams boric anhydride, 106 grams copper, and 120 grams aluminum, one-half in the form of powder, with cryolite as a flux and lime as a retarder to the reaction. This charge was heated 16 minutes in the horizontal arc furnace by a current of 350 amperes at 70 volts. The resulting ingot of metal was pulverized in an iron mortar, and treated for several days with hot nitric acid diluted by its own volume of water. After washing, the residue was treated by dilute hydrofluoric acid, and washed by water, alcohol, and ether. It was then dried as much as possible by the filter-pump, and heated for several hours in a drying oven. The residue consisted of aggregations of flat, dark crystals with a metallic lustre. Analysis showed the composition to be:

Molybdenum	63.4 per cent
Silicon	34.2 per cent.
Iron	1.1 per cent.
Boron	2.1 per cent.
	99.8 per cent.

Hot hydrofluoric acid dissolved some silicon and all the iron present. The residue from this treatment was unaffected by boiling aqua regia, but was completely soluble in a mixture of hydrofluoric and nitric acids. Table II shows that hydrofluoric acid is without action upon the boride of iron, therefore all the iron must be present as silicide; hence the boron is present as molybdenum boride. Iron boride was undoubtedly present in the original ingot, but was destroyed by the treatment with nitric acid. Since crystallization occurred in a

large amount of copper, there can be no free silicon present. After deducting the silicon required by the amount of iron present as FeSi_2 , and the molybdenum required by the boron, the residual molybdenum and silicon are far from the proportions required by the formula Mo_2Si_3 , but correspond closely with that required by the formula MoSi_2 . There is a slight excess of silicon even over the amount required by this formula.

The action of several reagents upon this substance is as follows:

Boiling nitric acid.	No action.
Boiling aqua regia.	No action.
Boiling hydrofluoric acid.	No action.
Fused sodium carbonate.	Action with incandescence.
Fused sodium nitrate.	Slow, but complete decomposition.

Its specific gravity is 6.31 at 20.5°C .

An earlier experiment in which a mixture of molybdenite and silica was reduced by calcium carbide, gave a similar result in the ratio of silicon to molybdenum.

While no pure silicide of molybdenum has been isolated in this experiment, the only way that the writer can explain the content in silicon is by the presence of a silicide of molybdenum richer in silicon than Mo_2Si_3 , and probably having the formula MoSi_2 .

BORIDES.

The preparation of silicides by the method proposed having been successfully accomplished, it seemed reasonable to suppose that the borides might be readily prepared by the same treatment, and a series of experiments was conducted with that end in view.

Molybdenum Boride.



A charge of 94 grams molybdenite, 41 grams boric anhydride, and 47 grams aluminum powder was heated in the arc

furnace for ten minutes with a current of 450 amperes at 60 volts. The result was 39.5 grams of somewhat brittle, white metal that scratched quartz. It was attacked by hot nitric acid and was completely dissolved by hot aqua regia. A qualitative test indicated that it contained boron in some quantity. Analysis proved its composition to be:

Molybdenum.....	85.3 per cent.
Iron	8.8 per cent.
Silicon.....	1.2 per cent.
Boron (by difference)	4.3 per cent.

The product, then, contained only 1.7 grams boron out of a total of 12.8 grams in the charge, and consisted of molybdenum boride dissolved in a large excess of molybdenum.

Chromium Boride.

A mixture of 300 grams potassium dichromate, 200 grams of borax, 800 grams of calcium carbide, 100 grams of aluminum, and 20 grams of fluor spar was heated 55 minutes with a current that averaged 360 amperes at 75 volts. The resulting slag was not acted on by water. The metallic product, weighing 66 grams, was of a dull white color, and cut quartz readily. On standing in air several days, it cracked in many places. Nitric acid had no visible effect upon it, but in hot hydrochloric acid there was a slow evolution of a gas of very disagreeable odor. This gas was probably hydrogen with traces of acetylene and boron hydride. Chromium and boron were found in the solution, which, after several days, was complete. Cold hydrofluoric acid had no visible effect even when nitric acid was added to it. Analysis indicated 7.0 per cent. iron, 0.9 per cent silicon, 1 per cent. carbon, 4 per cent. boron, 78.9 per cent. chromium, and aluminum which was not determined.

As it was thought that the bad odor of the gas evolved was due to the presence of a trace of an aluminum boride, which by treatment with acids yielded boron hydride, the experiment was repeated, with the aluminum omitted and 30 grams of car-

bon added in its place. The result was 130 grams of a very brittle, crystalline metal that failed to scratch quartz. Nitric acid did not act on it, and hydrochloric acid acted only slowly when hot. The gas evolved had no noticeable odor. Hydrofluoric acid at 60°, either alone or with the addition of nitric acid, had but a very slight action upon it. Analysis gave iron 9.0 per cent., chromium 78.9 per cent., silicon 0.2 per cent., carbon 5.0 per cent., boron 1.8 per cent.

The first of these products was a ferro-chromium-boron alloy, and the second, a ferro-chromium-carbon alloy. The iron in each case came from the "carbide," in which 0.6 per cent. would be sufficient to account for the iron found in the products.

Manganese Boride.

A Goldschmidt charge consisting of manganese dioxide, boric anhydride, and powdered aluminum in theoretical proportions was placed within a Hessian crucible, and this was placed inside a strong steel cylinder,⁴⁴ packed with powdered quartz. The cover was tightly bolted on, and the charge ignited by the electric current. The result was an ingot of metal weighing 25 grams, a yield of 72.2 per cent. of the total manganese and boron in the charge. Analysis proved its composition to be:

Manganese	71.7 per cent.
Silicon	1.0 per cent.
Iron	4.0 per cent.
Boron (by difference)	23.3 per cent,

The iron came from the fuse wire by means of which the charge was fired. The metal was finely crystalline, and *strongly magnetic*.

The product was, then, a mixture of the two borides of man-

⁴⁴ This apparatus was devised by Prof. C. F. Burgess for firing Goldschmidt charges under great pressures, and was placed by him at the disposal of the writer.

ganese, MnB and MnB_2 , with the boride of iron. The boride of iron is probably magnetic, although no statement in regard to this is made by Moissan. It is, however, remarkable that so small an amount (4.5 per cent.) should render the whole mass magnetic. It should be noted that manganese appears to be the essential ingredient in the magnetic alloys formed from non-magnetic metals.⁴⁵

Other experiments by this method, yielded similar results.

BORIDES AND SILICIDES BY ELECTROLYSIS.

Several experiments were tried to test the possibilities of employing an electrolytic method of preparing these compounds.

The first electrolysis attempted was that of borax with the addition of cryolite, carried out in the vertical furnace. The container was a section of 4-inch iron steam-pipe, five inches high, resting upon a magnesite brick in the center of which was the iron cathode. The charge was melted by striking an arc from a graphite anode, which was changed for a bar of wrought iron $1\frac{1}{4}$ inches in diameter as soon as the charge was fluid. The electrolysis was conducted with a current of 300 amperes. Metallic globules rose to the surface and burned brightly. The iron anode was rapidly consumed, and in 25 minutes, about 5 inches of it had melted away.

The resulting metal could be broken by severe pounding with a hammer. The fracture was quite different from that of either wrought iron or cast iron. Analysis gave 94.6 per cent. iron, 1.5 per cent. silicon, 1.5 per cent. carbon, 2.5 per cent. boron. Moissan has shown that iron containing 10 per cent. of boron is more fusible than cast iron. In this experiment, the iron evidently melted as soon as sufficient boron, carbon, and silicon had united with it to lower its fusing point to the temperature of the bath.

The experiment was repeated with a weighed iron anode which in 22 minutes lost 533 grams for 73.7 ampere hours.

⁴⁵ R. A. Hadfield, Chem. News, 90: 180 (1904). Dr. Hensler, Electrotechnische Zeitschr., March 2, 1905.

This is seven times the amount of iron dissolved by the same current by electrolysis in solutions. This current is the equivalent of 10 grams of boron, so that the product probably contained 1.8 per cent. boron. Similar results were obtained by the electrolysis of glass with an iron anode.

Wishing to learn whether the position of the electrodes had any influence upon the electrolysis or not, an experiment was conducted with horizontal iron electrodes a foot apart. The anode lost 121 grams, and the cathode 118.5 grams for 194 ampere hours, a loss per ampere hour of only 8 per cent. of that when the anode was directly above the cathode.

In these experiments, then, the reduction of the borax or the silica seems to be due to a secondary reaction of the metal liberated at the cathode, and not to a direct liberation of the non-metal at either the anode or the cathode. With an iron anode, the resulting alloy contains between one and three per cent. of boron. Metals whose borides and silicides are more infusible than those of iron ought to yield richer alloys.

SILICOBORIDES.

After three years of experimental research with the electric furnace, Moissan said:⁴⁶ "At high temperatures we have a simple chemistry, and we obtain only a single combination, always of a simple formula." It is seen from Table II that this statement is true of the majority of the borides and the silicides even down to the present.

On the other hand, there is evidence to show that ternary compounds can exist even at the temperatures of the electric furnace. In "siloxicon" ($\text{Si}_2\text{C}_2\text{O}$), discovered by Acheson, and the double carbide of tungsten and chromium ($\text{W}_2\text{C}_3\text{Cr}_3\text{C}_2$),⁴⁷ we have what appear to be definite chemical compounds of three elements. The production of any ternary compound in the electric furnace renders it at least possible that there shall ultimately be obtained several series of such substances, just as there are now known several series of binary compounds.

⁴⁶ *Ann. de Chim.*, 9: 277 (1896).

⁴⁷ Moissan, *C. R.*, 137: 292 (1903).

The names silicoboride and borosilicide were applied as early as 1893 to complex products of the electric furnace containing among other elements boron and silicon, but no definite chemical compounds had been isolated. Several facts seemed to the writer to point to silicon and boron as promising elements with which to form a ternary metallic compound. They each unite readily with many metals, to produce substances of remarkable stability, and they also unite with each other. The attempt was accordingly made to isolate a definite compound containing a metal, boron, and silicon.

Iron, chromium, nickel, and cobalt were selected as the most promising and convenient metals with which to experiment.

Ferrie oxide was prepared from electrolytic iron. With 100 grams of this was mixed 60 grams of pulverized borax glass prepared from pure borax, 72 grams silica, 114 grams powdered aluminum, 60 grams ingot aluminum, 70 grams copper as crystallizing medium, and 100 grams of cryolite. This mixture was heated 14 minutes in the electric furnace at an average of 26.7 kilowatts. The result was 135 grams of hard crystalline metal that could be broken only with much difficulty. As nitric acid acted on it only very slowly, it was heated with 115 grams more of copper, and 175 grams of aluminum. The product from this was crushed in an iron mortar, heated for six days in 50 per cent. nitric acid, repulverized, and the treatment with nitric acid continued two days more. As a qualitative test indicated the presence of copper, the substance was again ground in the iron mortar, and the treatment with nitric acid continued. By the microscope it was found that the resulting powder did not consist of definite crystals, but of irregular metallic fragments. It was strongly magnetic and contained boron. Analysis showed its composition to be:

Iron.....	72.3 per cent.	Cu ₂ Si.....	1.22 per cent.
Silicon ...	17.2 per cent.	Cr B.....	4.36 per cent.
Copper.....	1.0 per cent.	Fe B.....	35.3 per cent.
Chromium ..	3.6 per cent.	Fe ₂ Si.....	26.48 per cent.
Boron (by diff'ce).	5.9 per cent.	Fe Si.....	31.82 per cent.
	100.0 per cent.		99.2

The absence of any free silicon was assured by the large amount of copper in which it was crystallized. The presence of chromium was explained by the softening of part of a chromite brick in the furnace.

A formula for an iron silicoboride can be computed from this analysis as follows:

Per cent divided by atomic weight.					
Iron.....	72.3	per ct.	76.5	per ct.	1.366
Silicon.....	17.2	per ct.	18.0	per ct.	.643
Boron.....	5.14	per ct.	5.5	per ct.	.500
	94.64	per ct.	100.5	per ct.	

$$\left. \begin{array}{l} 1.366 \\ .643 \\ .500 \end{array} \right\} \times 6 = \left\{ \begin{array}{l} 8.1 \\ 3.85 \\ 3.00 \end{array} \right. \text{ or } \text{Fe}_{8.1}\text{Si}_4\text{B}_3$$

Another portion of the original ingot was treated for a week with hot aqua regia, being reground during this treatment. The residue was still magnetic, and contained boron as well as a trace of copper. The microscope showed that the substance was homogeneous. It would seem to be either an iron silico-boride, or a solidified solution of $\text{Fe}_2\text{Si}_3\text{FeSi}_3\text{FeB}$. Its magnetic and chemical behavior support this view. Fe_2Si is magnetic and is readily attacked by aqua regia. FeB is probably also magnetic, and is dissolved by either nitric acid or aqua regia. FeSi is non-magnetic and insoluble in both acids. From the magnetic properties of the substance, from its appearance under the microscope, and the treatment by acids to which it was subjected, it would seem impossible that these three compounds should exist separately in the residue.

Eight other experiments were tried, mainly with electrolytic iron as the source of that element. The results varied greatly. In several cases the product was completely soluble in nitric acid. In others, the residue obtained oxidized so readily while drying that it could not be obtained pure, even by washing with much alcohol and ether. Further experiments, for which time is at present lacking, are needed to establish beyond doubt the existence of a silicoboride of iron.

Nickel oxide, by a similar process, yielded a metallic residue containing 21.0 per cent. silicon and 11.45 per cent. iron. The source of the iron was found to be an impure nickel oxide.

Five experiments with pure nickel oxide were unsatisfactory, as the product was completely dissolved by nitric acid.

Tungstic acid, silica and boric anhydride were reduced in the presence of copper, but the product was entirely dissolved by nitric acid. This is a surprising result, as the silicide of tungsten is completely insoluble, and the boride only slightly attacked by this acid.

Similar experiments were tried with molybdic acid, but with unsatisfactory results.

More encouraging results were obtained from potassium dichromate, but further investigation is needed upon this.

Although these experiments have failed to yield a series of silicoborides, the writer does not yet regard such a series of compounds as impossible. The failure may be due to the method used, which is not suited to the production of compounds of the metals with boron. It is the writer's intention to take up this investigation again at the earliest opportunity, using the method of synthesis from the elements.

VI.

ELECTRICAL AND OTHER DATA CONCERNING THE ARC FURNACE.

In this series of experiments many observations were made upon the length of arc, its variation in resistance, electrode consumption, etc. Some of these observations are included here as of interest, and perhaps of value to other experimenters.

The longest arcs obtained were 15.5 and 14.4 cm. ($6\frac{1}{2}$ and $5\frac{11}{16}$ inches) at 104 volts, the former at 800 amperes. At the usual voltage of 80 on the furnace terminals, the length of arc for 600 amperes varied from 6 to 7.5 cm. ($2\frac{3}{8}$ to 3 inches) as a rule.

Resistance of the arc depends upon:

a. Length.

b. Current strength. (See Table VI.)

Increase of current increases the cross section of the arc.

c. Temperature of the furnace.

During the rise in temperature at the beginning of an experiment the arc must be gradually lengthened if the current is to be maintained constant. When a cold charge is fed into a hot furnace the current is diminished.

TABLE VI.—*Effect of varying currents upon the resistance of the arc*

No. of Experiment.	Amperes.	Volts.	Resistance.	$R_1:R$
98	600	75	.118	1
	360	75	.202	1.71
	{ 210	79	.369	3.12
	{ 190	82	.425	3.60
	{ 150	81	.533	4.51
	{ 140	83	.586	4.96
	{ 120	79	.651	5.51
	{ 120	81	.668	5.66
	{ 100	81	.803	6.80
	{ 70	80	1.136	9.62
	{ 55	85	1.538	13.03
	{ 40	92	2.293	19.43
111	580	78	.127	1
	{ 400	72	.173	1.36
	{ 330	77	.226	1.78
	{ 280	77	.266	2.09
	{ 200	81	.398	3.14
	{ 160	81	.499	3.93
	{ 200	76	.373	2.94
	{ 180	66	.359	2.83
	{ 150	77	.568	3.18
	{ 120	75	.618	4.87
	{ 130	75	.569	4.48
	{ 120	70	.576	4.53
	{ 120	70	.576	4.53
	{ 110	71	.638	5.02
	{ 75	83	1.099	8.66
	{ 70	80	1.136	8.95
	{ 80	89	1.105	10.97

d. Quantity and nature of vapors within the furnace.

An increase in the amount of vapors of sodium and of silicon lowers the resistance. Possibly there are vapors which are capable of increasing the resistance. (See Table VII.)

The data of Table VI were taken at the close of experiments when the furnace was very hot. Maintaining the length of arc unchanged, the current was cut down by increasing the external resistance. The pairs of bracketed readings were made about ten seconds apart with the same resistance in the circuit. An entire set of readings occupied about three minutes, so that the temperature within the furnace was practically constant. The column $R_1 : R$, shows the increase in resistance of the arc as the current is diminished and the external resistance is increased. Curves from Table VI are shown in Figure 2.

From the above and other similar data, the writer draws the conclusion that *the arc tends to maintain a constant ratio between its own resistance and that of the remainder of the circuit, or an arc of fixed length tends to maintain a constant voltage.*

In experiment 111, the external resistance was varied about 900 per cent., the maximum variation in voltage of the arc was 14.1 per cent., and the average, only 1.8 per cent. The rise in voltage seen in the last readings, occurred but a few seconds before the arc died out. One readily pictures the shrinking of the arc to a mere pencil of carbon vapor as the current is diminished.

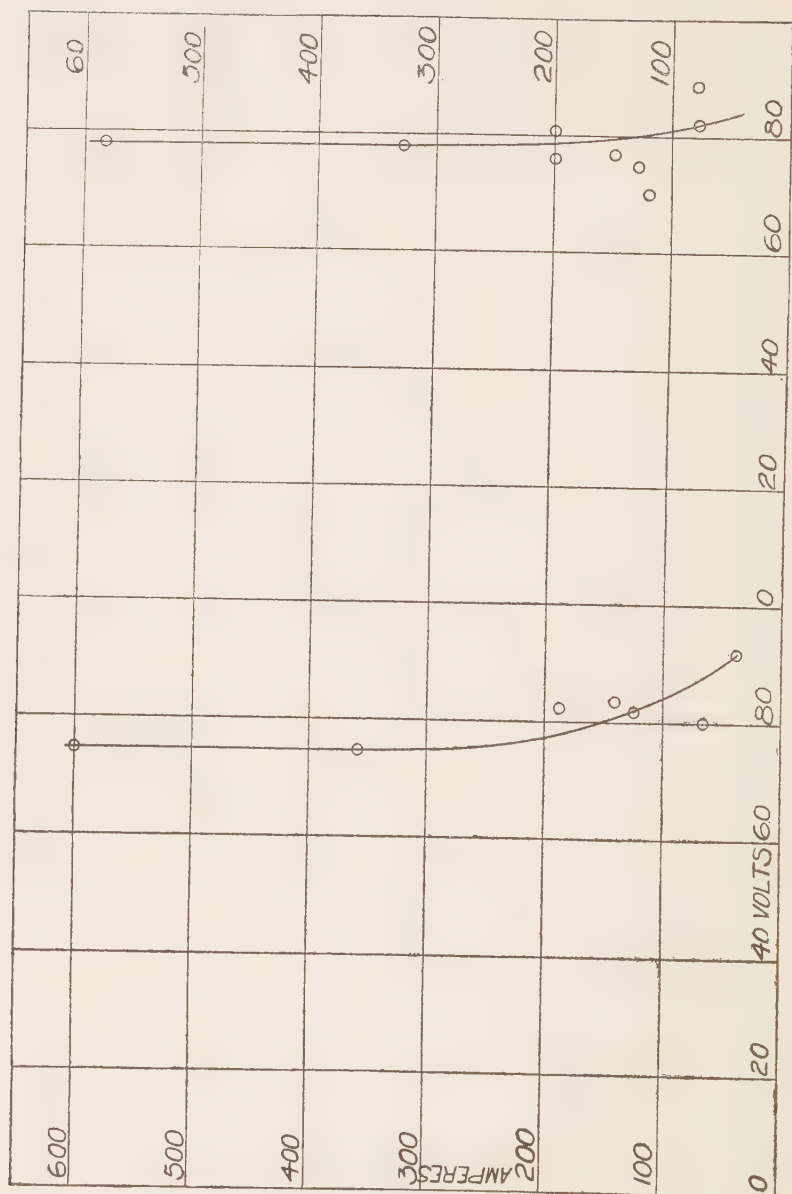


FIGURE 2.—Curves of Resistance, from Table VI.

TABLE VII.—*The effect of vapors upon the resistance of an arc of constant length.*

No. of experiment.	Amperes.	Volts.	Resistance.	Change in resistance. Per cent.	
20	350	75	.214		Silicon vapor suddenly formed.
	400	68	.170	—20	
118	160	82	.512		Yellow flame suddenly appeared.
	300	65	.216	—59	
	230	75	.239	—53	
126	250	82	.328		Little flame. Much flame. No flame.
	300	75	.250	—24	
	230	80	.348	+ 9	
132	640	72	.113		Much flame from furnace Flame continued. Flame instantly ceased. Flame started again. Flame continued.
	600	74	.123	+ 9	
	500	81	.162	+42	
	560	77	.138	+22	
	570	77	.135	+19	

The above records were made after the vigor of the chemical reaction was over, for at the height of the reaction, the fluctuations of the instruments were usually too rapid to be read.

Comment upon these figures is scarcely necessary. It will be readily seen that the effect of vapors may in some cases demand reckoning upon.

FIGURE 3.—Curious Electrical Phenomenon.



TABLE VIII.—*General Data Concerning the Arc Furnace.*

Exp. No.	Diam. of Electrodes.	Average K. W.	Time in Min.	K. W. x Min.	Volts.	Amp.	Length of Arc.		Resistance.		
							Inches.	C. M.	Total.	Per inch.	Per cm.
129	1½	28.0	36	1008	104	800	61⅞	15.5	.123	.020	.0079
61	1¼	30.5	12	366	80	600	33¼	9.5	.126	.034	.0132
121	1½	28.6	30	859	81	550	31⅞	9.6	.141	.037	.0147
123	1½	28.6	61	1521	78	570	3	7.7	.130	.043	.0169
88	1¼	24.2	28	696	78	560	23¼	7.0	.133	.048	.0190
150	2	21.8	45	980	68	650	2	5.05	.098	.049	.0194
86	1¼	33.3	15	500	75	600	21¼	5.7	.118	.055	.0207
89	1¼	18.1	38	687	70	400	27⅞	7.3	.168	.058	.0230
99	1¼	28.7	14	402	76	600	2	5.05	.120	.060	.0238
09	1¼	26.0	25	670	80	550	21⅞	5.4	.138	.065	.0255
04	1¼	31.1	8	249	79	550	13¼	4.4	.118	.068	.0268
94	1¼	24.7	10	247	82	500	2⅝	5.6	.157	.072	.0280
100	1¼	26.1	14	414	78	600	11⅞	4.3	.123	.073	.0286
107	1¼	29.9	23	482	80	300	27⅞	7.3	.259	.090	.0350
127*	1½	28.1	45	1264	103	150	51⅞	14.4	.679	.119	.0470

* The current was cut down from 400 amperes to 150 by drawing out the arc instead of increasing the external resistance as usual. This is responsible for the abnormal resistance found.

The effect of an increase of current in lowering the resistance of the arc has already been pointed out; the other factor appears to be the temperature, estimating this from both the average, and the total energy delivered to the furnace.

As has been already stated, the source of trouble when the arc is unsteady is to be found at the anode, and seems to the writer to be due to insufficient heat to maintain there a layer of carbon vapor. A very interesting phenomenon was twice observed with an alternating arc; namely, that the electrodes interlocked, as shown in full size drawing, Figure 3.

There is a deposition upon as well as a vaporization of each electrode. The points of each are coated with smooth, lustrous graphite of extremely fine grain. There are two separate arcs. Each half of the current wave has its own exclusive territory on the electrodes. Each arc dies out with reversal of current; yet sufficient carbon vapor remains in its crater so that when this electrode is once more anode, the path of least resistance is from the crater rather than from any other part of the electrode. This phenomenon occurred only with a low voltage and large electrodes, and would seem to be possible only when the crater of the anode during each phase is small in comparison with the area of the end of the electrode.

Observations were made upon the loss in weight of graphite electrodes during several experiments. The results are given in Table IX.

TABLE IX.—*Loss in weight of electrodes.*

	Exp. No.	Diameter of electrode Ins.	Time.	Average K. W.	K. W. x time.	LOSS IN GRAMS.								
						Total.		Ratio.	Per minute.		Per average K. W.		Per K. W. minute.	
						Anode.	Cathode.		An.Cath.	Anode.	Cathode.	Anode.	Cathode.	Anode.
A. C.....	150A	1	37	6.9	229	17	14.3	1.19	.46	.40	2.40	2.35	.074	.062
A. C.	151B	1	60	11.6	695	28.8	19.6	1.47	.48	.32	2.48	1.69	.041	.028
D. C.....	151A	1	9	13.4	120	11.3	2.02	5.13	1.24	.23	.84	.16	.094	.019
	139	1½	22	23.7	632	16.3	20	.81	.71	.87	.59	.72	.026	.031
	136	1½	58	25.1	1,457	59.3	32	1.87	1.02	.55	2.33	1.23	.040	.022
	138	1½	39	32.2	1,266	54.2	17	3.19	1.39	.44	1.68	.52	.043	.013
	137	1½	55	28.4	1,561	82.2	43	1.93	1.51	.78	2.91	1.51	.053	.028
	140	1½	22	23.7	523	49.0	15	3.27	2.23	.68	2.07	.63	.095	.029
Average.						52.3	25		1.37	.66	1.92	.92	.051	.025
	152	2	57	20.8	1,186	103.8	37.6	2.72	1.82	.66	4.98	1.81	.105	.038
	148	2	27	31.3	845	166.2	70.2	2.37	6.20	2.96	5.31	2.24	.197	.083
Average.						135	53.9		4.01	1.81	5.15	2.03	.151	.061
Furnace filled with illum- inating gas.	141	1½	38	31.4	1,142	23.5	10.4	2.26	.62	.27	.76	.33	.021	.009
	150	2	45	21.8	980	42.8	15.9	2.69	.95	.35	2.00	.73	.043	.016
	155	2	64	26.5	1,894	82	73	1.12	1.34	1.14	3.09	2.75	.043	.038
	151	2	46	14.2	656	56.1	9.3	6.03	1.22	.20	3.95	.65	.085	.014
	147	2	22	19.5	430	40.8	32	1.27	1.85	1.45	2.04	1.60	.085	.074
Average.						55.4	32.5		1.34	.78	2.77	1.43	.066	.035

Direct current was used in all except the first two experiments. These are marked A. C. and to them the terms anode and cathode do not apply. In these the electrode losing the more in weight extended into the furnace much farther than the other.

Electrode losses seem to be due to three causes:

1. Volatilization from the crater, confined to the anode.
2. Oxidation.
3. Disintegration—particles fall from the electrodes.

(1) is independent of, (2) and (3) dependent upon, the length of electrode within the furnace. The total loss is diminished about 50 per cent. by filling the furnace with illuminating gas; this can diminish only (2) and (3). The losses with 2-inch electrodes were double those with $1\frac{1}{2}$ inch diameter. This points again to the use of the smallest possible electrodes. It should be stated, however, that only a single pair of two inch electrodes were tested.

VII.

CONCLUSION.

The results obtained by this series of experiments are the following:

1. The proposed method of preparing the borides and the silicides of the metals by the simultaneous reduction of the oxygen compounds of both elements is not suited to the preparation of the borides, but can be used successfully for the silicides.

2. The existence of a new silicide of molybdenum has been indicated.

3. An investigation of the possibility of a new series of electric furnace products, the silicoborides, has been made. Although the experiments indicate the existence of such a com-

pound of iron, they must still be regarded as merely preliminary. The results with chromium and molybdenum were encouraging, but by no means conclusive.

4. Data concerning the arc furnace heretofore unpublished, have been obtained.

In addition to these experimental results, it is believed that Tables II and III, which have been found most convenient for reference during these researches, may prove a useful contribution to the literature of the borides and the silicides, and that the method of firing "Goldschmidt charges" in the electric furnace, discovered during these experiments, will prove very valuable in special cases.

APPENDIX.

In the interval between the completion of this thesis and its publication, two new borides, ThB_4 and ThB_6 ,⁴⁸ and a new silicide of copper, Cu_4Si ,⁴⁹ have been prepared, and the data concerning them have been incorporated in Table II. Two articles have also been published which touch upon the principal problem of this thesis, namely the preparation of metallic borides and silicides from their oxygen compounds, thus avoiding the difficulties attending the isolation of boron and silicon. The method used in both cases was that of reduction by powdered aluminum, but without the use of the electric furnace.

In the first case⁵⁰ a mixture of the metallic oxide, the non-metal, and aluminum was ignited by a magnesium cartridge. By this method two phosphides Fe_2P and Mn_2P_2 were prepared. In attempting the more difficult reductions of silica and boric anhydride, the oxide of copper or of tin with an equivalent amount of aluminum was added to the charge to supply the heat required to produce a good fusion. By this means an ingot of silicon-copper containing 10 per cent. silicon was obtained, and also the silicide of iron, FeSi . From the oxides of iron and boron an ingot was obtained which contained boron, concerning which the author remarks, "It is difficult to isolate a definite boride." All these products contained traces at least of aluminum. The idea of adding an extra quantity of aluminum and an equivalent amount of some harmless oxidizing material, here published for the first time, so far as the writer has observed, is a valuable advance in the applica-

⁴⁸ B. du Jassonneix, C. R., 141: 191-193 (1905).

⁴⁹ E. Vigouroux, C. R., 142: 87-88 (1906).

⁵⁰ A. Colani, C. R., 141: 33-35 (1905).

tion of aluminothermy to chemistry. The writer has independently applied the same idea to the reduction of tungsten oxide, using the alkaline-earth peroxides as the source of oxygen.

C. Matignon and R. Trannoy⁵¹ confirm the experiments of Colani in regard to the production of binary compounds by the aluminothermic method, and, in addition to a number of phosphides and arsenides, produced the silicides of manganese, chromium, copper, cobalt, nickel, and iron by inducing reaction in a strongly heated mixture of metallic oxide, silica, and aluminum. Borides of manganese and iron were similarly produced. In this case the high temperature necessary to the separation of the metallic product from the alumina, was secured by starting the reaction in a mass already heated to a high temperature.

These two series of experiments confirm the writer's conclusion that silicides may be readily prepared directly from silica by reduction with aluminum, and they further show that this can be done without the aid of the electric furnace. Since the production of silicon on a commercial scale by F. J. Tone of Niagara Falls this has become of minor importance. The production of the borides of manganese and iron by this method does not confute the writer's conclusion, that, as a general method, the simultaneous reduction of a metallic oxide and boron anhydride by aluminum is not suited to the production of metallic borides. It can be used successfully in the case of the easily reducible metallic oxides, but not for those of titanium, tungsten, and many others. The problem of obtaining the extra heat needed above that supplied by the reaction in such difficult reductions is a very interesting one, and is being approached from different points of view by many investigators in various parts of the world.

⁵¹ C. R., 141: 190.

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